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Reaction Kinetics of Ozone with Sulfur Compounds

Montana Univ, Missoula Dept of Chemistry

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Ecological Research Series

REACTION KINETICS OF OZONE WITH SULFUR COMPOUNDS

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The reaction between ozone, sulfur dioxide, dimethyl sulfide, methanethiol and dimethyl disulfide are reported.

The rate of reaction between ozone and dissolved sulfur dioxide is strongly pH dependent. These results suggest that under some conditions atmospheric oxidation of sulfur dioxide may involve ozone. Dimethyl sulfide was found to react rapidly with ozone in the gas phase but reproducible kinetic data were not obtained. Stoichiometric and yield data from the reaction between ozone and methanethiol or dimethyl disulfide in aqueous solution indicate those reactions to be complex mechanistically, although one product, methane sulfonic acid is predominant.

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REACTION KINETICS OF OZONE WITH SULFUR COMPOUNDS

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ABSTRACT

This report presents data on the reaction between ozone and several sulfur compounds which are air pollutants. The compounds of interest are sulfur dioxide, dimethyl sulfide, methanethiol and dimethyl disulfide.

The rate of the reaction between ozone and dissolved sulfur dioxide is strongly pH dependent. This is so because sulfite ion reacts extremely rapidly (second order rate constant four orders of magnitude higher than that of bi-sulfite ion). These results suggest that under some conditions atmospheric oxidation of sulfur dioxide may involve ozone.

Dimethyl sulfide was found to reaction extremely rapidly with ozone in the gas phase but reproducible kinetic data were not obtained.

Stoichiometric and yield data from the reaction between ozone and methanethiol or dimethyl disulfide in aqueous solution indicate those reactions to be complex mechanistically, although one product, methane sulfonic acid is predominant.

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SECTION I

CONCLUSIONS

The first significant scientific finding of the research carried out under this grant is that the rate of ozonation of sulfur IV in aqueous solution is controlled, almost exclusively, by the concentration of sulfite ion. Sulfite reacts about four orders of magnitude faster than bisulfite ion and at least two million times faster than aqueous sulfur dioxide.

However it is the absolute magnitude of the specific rate constant for the ozone-sulfite ion reaction which is of significance to the possible role which ozone might play in the atmospheric oxidation of sulfur dioxide. Our calculations show that under certain specified conditions, the most crucial of which is the presence of liquid water, ozone may play an important role in the atmospheric phase of the biogeochemical cycling of sulfur.

Methane thiol and dimethyl disulfide also react extremely rapidly with ozone in aqueous solution to yield methane sulfonic acid along with several minor products. The reaction is more complicated, in a mechanistic sense, than the sulfur IV-ozone reaction which is a simple second order reaction.

Gas phase kinetic studies for the reaction between ozone and dimethyl sulfide show the reaction to be extremely rapid and complex (mixed order) but too few data were obtained for meaningful comment.

SECTION II

RECOMMENDATIONS

The rate constants for the reaction between ozone and sulfur IV in solution which were obtained in this study should be considered in any model for the atmospheric oxidation of sulfur dioxide.

Since ozone is highly reactive with many subtances, including all negative ions which are oxidizable, and many positive ions in their lower oxidation states, it would be necessary to know both the concentrations of such ions in atmospheric water and their rates of reaction with ozone in order to establish a reasonable model. Such data are not available.

SECTION III

INTRODUCTION

GENERAL

Our original goal was to measure the rates of the reaction of ozone with sulfur dioxide and several malodorous sulfur compounds (mercaptans, sulfides, disulfides and hydrogen sulfide). Determinations were to be made in the gas phase for dimethyl sulfide and methyl mercaptan and in water for sulfur dioxide, methyl mercaptan and hydrogen sulfide. Several serious experimental problems and a shortening of the project period (from three to two funded years) resulted in a more modest set of achievements. We report here on a complete kinetic study of sulfur dioxide in aqueous solutions, on stoichiometric and product data of dimethyl mercaptan with ozone in water, and on the gas phase reaction of dimethyl sulfide with ozone.

SULFUR DIOXIDE-OZONE

The importance of sulfur dioxide in air pollution episodes is well documented. Recent reviews have covered the subject so well[1,2,3,4] that only a few references which are directly pertinent to the possible reaction of sulfur dioxide with ozone will be discussed here.

The reaction of ozone with sulfur dioxide has sparked some debate. Gregor and Martin's finding of sulfuric acid in the oxidation of hydrogen sulfide[5] (presumably through the further oxidation of sulfur dioxide) was not confirmed by Cadle when both reactants were in low concentration in the gas phase[6]. Pitts recommended in the "Technical Report on Air Quality Criteria for Photochemical Oxidants" by the State of California Department of Public Health that the ozone-sulfur dioxide reaction be studied in the presence of water[7]. Cadle suggested that such a study would be fruitless

but did comment that a study of the ozonation of sulfurous acid in fog droplets might be appropriate[8].

One very interesting study of the reaction of ozone with sulfur dioxide was carried out by Espenson and Taube[9]. Equation 1 describes the general stoichiometry of the reaction in water while the most intriguing discovery was that the sulfate formed contains up to two oxygen atoms from ozone.

equation (1) $$SO_2 + O_3 \overset{H_2O}{\rightleftharpoons} HSO_4^- + H^+ + O_2$$

While the work described in this report was in progress, two important papers were published on possible interactions between ozone, sulfur dioxide, and moisture. In the first, Cox and Pankett observed that both sulfur dioxide and ozone decay on the walls of containers, the rate increasing rapidly with increasing humidity[10]. In the second Pankett reported the rate of reaction of bisulfite ion with ozone at pH 5[11]. Since his work is directly comparable to ours, we will reserve discussion of that paper until later in this report.

DIMETHYL SULFIDE-OZONE

Dimethyl sulfide is a malodorous, water insoluble sulfide whose ozone oxidation products, dimethyl sulfoxide and dimethyl sulfone are relatively odorless and water soluble. Although the sulfide is not normally found in appreciable amounts in polluted air, its presence is definitely noticeable where Kraft pulp mills operate. Akamatsu's studies show that the recovery process losses plus blow gas emissions constitute the major sources although not the only source of a series of malodorous sulfur compounds.[12] Some idea of kinds of compounds found, the variability of concentrations, and the extent of the problem for dimethyl sulfide can be found in Table 1, taken from Akamatsu.

TABLE 1

GASEOUS SULFUR LOSS* BALANCE SHEET FOR SOUTHERN KRAFT MILL A

Source	Form of gas emission					Total, lb/ton	% from each source
	SO_2	H_2S	RSH	RSR	RSSR		
Recovery	6.71	12.97	3.98	2.01	0.04	25.71	85.00
Dissolving tank	0.07	0.04	0.15	0.06	0.01	0.23	1.10
Lime kiln	0.05	0.09	0.31	0.16	0.05	0.66	2.20
Digester	----	0.01	0.02	0.22	0.46	0.70	2.30
Blow tank	----	0.02	0.33	0.74	0.44	1.53	5.01
Pulp washer vent	0.01	0.01	0.18	0.01	0.01	0.19	0.60
Evaporator non-condensable	0.01	0.12	0.13	0.07	0.01	0.32	1.10
Bark boiler	0.16	0.67	0.01	0.01	0.01	0.83	2.70
Total	6.99	13.91	5.10	3.26	1.00	30.26	
% of total in each form of sulfur	23.10	46.00	16.80	10.80	3.70		100.00

* lb S--/ton airdried pulp.

TABLE 1 CONTINUED

GASEOUS SULFUR LOSS* BALANCE SHEET FOR SOUTHERN KRAFT MILL B

Source	Form of gas emission					Total, lb/ton	% from each source
	SO_2	H_2S	RSH	RSR	RSSR		
Recovery	1.20	3.61	0.30	0.00	0.15	5.26	41.90
Dissolving tank	0.00	0.02	0.07	0.02	0.00	0.11	0.90
Kiln	0.15	0.24	0.26	0.00	0.09	0.74	5.90
Digester	----	0.01	0.03	0.83	0.15	1.02	8.10
Blow	----	0.10	0.50	1.40	2.05	4.05	32.20
Evaporator	----	0.03	0.01	0.02	0.00	0.06	0.50
Tall oil Acidification	----	0.27	0.01	0.00	0.01	0.29	2.30
Neutralization	----	1.01	0.02	0.00	0.00	1.03	8.20
Total	1.35	5.29	1.20	2.27	2.45	12.56	
% of total in each form of sulfur	10.70	42.10	9.60	18.10	19.50		100.00

* lb S--/ton airdried pulp

The first reported ozonation of organic sulfides was in 1933, when Maneck[13] ozonized benzyl sulfide in CCl_4 and reported intitial reaction products to be the sulfoxide and sulfone. Prolonged ozonation oxidized these initial products to sulfuric acid, carbon dioxide, and benzoic acid.

In 1942, Bohme and Fischer[14] ozonized several organic sulfides, including dimethyl sulfide, in chloroform. A nearly quantitative yield of the sulfone was obtained for the compounds Me_2S, Et_2S, $(ClCH_2CH_2)_2S$, $MeS\emptyset$, $EtSCH_2\emptyset$, and $(\emptyset CH_2)_2S$. That the sulfoxide was formed as a precursor to the sulfone was shown by the isolation of benzyl sulfoxide from the sulfide when an insufficient amount of ozone was used. For some sulfides, i.e., chloromethyl ethyl sulfide, the sulfoxide was the final product.

While studying the possibility of the use of ozone as a titrimetric agent for quantitative determination of olefinic unsaturation in petroleum fractions, Boer and Kooyman[15] ozonized several sulfides to determine the effect of their presence in the olefinic mixtures. The dialkyl sulfides were reported to consume from $\frac{1}{4}$ to $\frac{3}{4}$ mole of ozone per mole of sulfur compound. Benzothiophene consumed exactly one mole of ozone, while thiophene and dibenzothiophene did not interfere with the reaction.

In 1954, Bateman and Cunneen[16] studied the autoxidability of several monosulfides at temperatures ranging from 45°-75°C and found that saturated alkyl and phenyl sulfides absorb no oxygen during 24 hours at 75°. Similarly inert were the benzyl and diphenylmethyl substituted sulfides.

While the benzyl sulfides undergo photo-oxidation, the dialkyl sulfides oxidized only when catalyzed by $\alpha\alpha'$-azobis-isobutyronitrile. The diphenyl sulfides were inert to all autoxidation.

Barnard[17] found that monosulfide-ozone reactions in solution at -25°C yielded not only the sulfoxide and sulfone but other products as well. For the reaction:

$$R' \cdot S \cdot R'' + 2O_3 \rightarrow R'' \cdot SO_2 \cdot R'' + 2O_2$$

less than the theoretical amount of ozone was needed for a nearly quantitative yield of the sulfone. The ozonation, run just to completion, of di-n-butyl sulfide gave a 100% yield of the sulfone "smelling of butyraldehyde and butyric acid and reacting acid to litmus". The reactivity of the sulfides indicated that the most easily oxidized sulfides required the least ozone.

Since saturated alkyl sulfides and several aryl sulfides are inert to molecular oxygen without a catalyst, Barnard speculated that the ozone must either catalyze the sulfide-oxygen oxidation or produce, after loss of an oxygen atom, activated oxygen molecules some of which participate in the oxidation of the sulfide or sulfoxide.

Barnard's ozone uptake curves indicated that oxidation occurs in two stages to give first the sulfoxide and then the sulfone. By following the ozonolysis of cyclohexyl methyl sulfide with infrared spectroscopy, he was able to show that at least 98-99% of the sulfide was converted to the sulfoxide before any sulfone was detected. This indicates the rate of sulfoxide formation is 50-100 times faster than that of the sulfone.

More recently, Maggiolo and Blair[18] found that ozone reacted with dialkyl and diaryl sulfides according to the equation:

$$R_2S \xrightarrow{O_3} O_2 + R_2SO \xrightarrow{O_3} R_2SO_2 + O_2$$

When the reaction was run in a nonpolar solvent, it was found to be stoichiometric for the aliphatic and aromatic sulfoxides and for the aliphatic sulfones.

$$\text{Ø-CH}_2 \cdot \text{S} \cdot \text{CH}_2\text{-Ø} + \text{O}_3 \xrightarrow[20°\text{C}]{\text{CHCl}_3} \text{Ø-CH}_2 \cdot \overset{\text{O}}{\underset{}{\text{S}}} \cdot \text{CH}_2\text{Ø}$$

10.7g	2.33g	11.3g
(.0499)	(.0485)	(.0491)

$$\text{Ø-CH}_2 \cdot \text{S} \cdot \text{CH}_2\text{-Ø} + \text{O}_3 \rightarrow \text{Ø-CH}_2 \cdot \overset{\text{O}}{\underset{\text{O}}{\text{S}}} \cdot \text{CH}_2\text{-Ø}$$

10.7g	4.71g	12.0g
(.0499)	(.0981)	(.0487)

Horner, Schaefer and Ludwig[19] also found that sulfides react in ethyl chloride with ozone according to Maggiolo and Blair's equation to give sulfoxides and sulfones in 80-100% yield.

Six years later, work by Hughes, McMinn, and Burleson[20] lent still further support to Maggiolo and Blair's stoichiometry by obtaining stoichiometric yields of sulfoxide and sulfone when Bis (B-Hydroxyethyl) sulfide was ozonized at 100°C.

Research was carried out in this laboratory on the ozonation of dimethyl sulfide in methylene chloride at -78°C. Nuclear magnetic resonance analysis of aliquots taken during the reaction revealed dimethyl sulfone formation after only 1% of the reaction was completed. While this would seem to indicate a DMSO/O_3 reaction considerably faster than that

for DMS and ozone, it is also possible, due to poor mixing in the reaction vessel, that pockets of high ozone concentration could occur and that the sulfone resulted from the slow oxidation of the DMSO trapped in these areas. Product analysis indicated an uptake of 1.86 moles of ozone per mole of sulfide for conversion to the sulfone.

Not until 1966 was there any work done on the vapor phase ozonation of dimethyl sulfide. In that year, pollution control work resulted in two studies by Akamatsu, et. al.,[21] on the removal of dimethyl sulfide from pulping processes by vapor phase ozonation. This work showed that dimethyl sulfide oxidized with oxygen containing 7% ozone gave 75% dimethyl sulfoxide and 25% dimethyl sulfone. Another project of Akamatsu[12] showed that an 85% yield of the sulfoxide could be obtained when dimethyl sulfide and oxygen containing 20% ozone were fed into a reactor in a 3:7 ratio at 30°C.

Hales[22] studied the gas phase kinetics of hydrogen sulfide with ozone. The results of that study have only an indirect bearing on the reaction of ozone with dimethyl sulfide, but the methodology seemed to be particularly useful to the study we planned to carry out.

THIOLS AND DISULFIDES-OZONE

The first ozone oxidation of a thiol was reported in 1933 by Martin Maneck[13]. He ozonized ethanethiol and obtained ethanesulfonic acid. The conversion of thiols to sulfonic acids has also been observed by several other authors. Asinger and coworkers[23] used ozonation of thiol to prepare a number of long chain aliphatic sulfonic acids in yields from 70 to 100%. Barnard[17] reported quantitative conversion of thiophenol to benzenesolfonic acid. The conversion of isobutanethiol to isobutanesulfonic was accomplished with a 90% yield by Erickson[24].

Both Barnard and Erickson have determined the stoichiometry involved. Barnard[17] found that 1.6 moles of ozone per mole of thiophenol were absorbed when the reaction was carried out by adding ozonized oxygen to a CCl_4 solution of the thiol maintained at -20°C. Working in methanol at -78°C Erickson[24] found a stoichiometry of 1.6:1 when an ozone-oxygen stream was used and a stoichiometry of 3.3:1 when an ozone-nitrogen stream was used for the conversion of isobutanethiol to the corresponding sulfonic acid.

Disulfides and thiolsulfonates have been reported as minor products of the reaction. Maneck[13] found both. In Erickson's[24] work the disulfide was formed, but the thiolsulfonate was not identified. However, all the minor products were not identified. Erickson also found methyl isobutanesulfonate, a product that must have arisen through a reaction with the solvent (CH_3OH). An ozonation of thiophenol performed by Maneck[13] yielded no sulfonic acid. The only products were the corresponding disulfide, thiolsulfonate and disulfone. Maneck also noted that continued ozonation of either ethanethiol or thiolophenol resulted in an attack of the carbon-sulfur bonds and the formation of sulfuric acid.

The mechanism of the ozone-thiol reaction has hardly been considered. Maneck[13] offered the following equations, but he gave no proof for them.

$$EtSH + O_3 \rightarrow EtSO_3H \quad (22)$$

$$2EtSH + O \rightarrow EtSSEt + H_2O \quad (23)$$

$$EtSSEt + 2O \rightarrow \underset{\underset{O}{|}}{EtSSEt} \quad (24)$$

At that time thiolsulfonates were believed to have a disulfoxide structure and the thiolsulfonate was reported as a disulfoxide.

Two studies of the ozone-thiol reaction in the gas phase have been carried out. The use of ozone to control Kraft

pulp mill odors has been considered by Akamatsu[12]. He found that methanethiol was converted to an odorless, water-soluble compound.

A kinetic study of the ozone-ethanethiol reaction in the gas phase was performed by Kirchner, Kastenhuber and Biering[25]. Concentrations were in the parts per million range and under those conditions the reaction proceeded with carbon-sulfur bond cleavage. The kinetics were determined by competitive reactions with hexene and isobutene. At 30°C a rate constant of $2.4 \pm 0.8 \times 10^3$ l/mole sec was found.

A series of disulfides has been ozonized by Barnard[7]. The reactions were carried out in carbon tetrachloride at -25°C. Sulfonic anhydrides and thiolsulfonates were the major products. Disulfones were also formed in small quantities. His results are summarized in Table II. Dimethyl and dibenzyl disulfide were atypical. Dibenzyl disulfide reacted by giving carbon-sulfur bond cleavage. Dimethyl disulfide gave abnormal product ratios. He proposed that the reaction proceeds according to the following scheme:

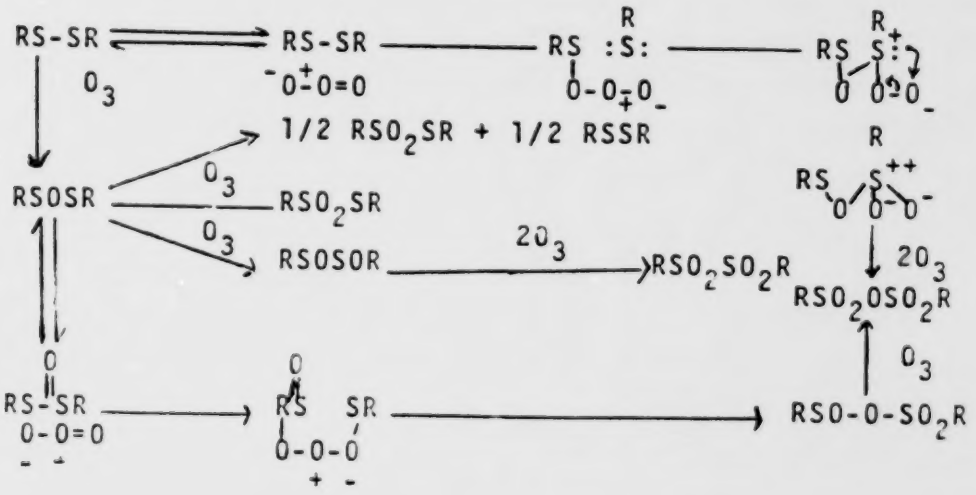


TABLE II

PRODUCTS OF OZONOLYSIS OF DISULFIDES[17]

R	O_3 Absorbed (moles)	Sulfonic Anhydride (%)	Thiolsulfonate (%)
Ph	2.6	90	6
p-Cl C_6H_4	2.9	84	10
n-Bu	2.6	80	10
Me	2.0	39	50
CH_2Ph	5	--	--

Horner et. al.[19] have ozonized some of the same disulfides as Barnard. The reactions were done in ethyl chloride and they obtained different results. Horner obtained an 82% yield of benzyl phenylmethanethiolsulfonate from dibenzyl disulfide. Diphenyl disulfide also gave its thiolsulfonate, but only in 23% yield. The product from ozonation of di-n-butyl disulfide decomposed and was not identified.

SECTION IV

EXPERIMENTAL METHODS
OZONE-SULFUR DIOXIDE AQUEOUS PHASE KINETICS

INSTRUMENTAL METHOD

We determined the rate of ozonation of total sulfur species present in buffered aqueous solutions of sulfur dioxide at variable pH by a stopped flow technique. The stopped flow system used was an Aminco-Morrow stopped flow spectrophotometer with associated ultraviolet source and a Biomation transient recorder Model 610 with a Cathode Ray Tube display. The transient recorder storage was then fed into a Bausch and Lomb VOM-10 recorder. This enabled the signal collected over a few milliseconds to be recorded on a 10 second virtual time base for a permanent record, rather than photographing the CRT display. The log mode (0-1 Absorbance units on the oscilloscope and transient recorder) was used on all runs. Five traces were recorded with each run and three runs were made with each pair of reactant solutions.

TEMPERATURE REGULATION

A large (4 gal.) water bath was used with a cooling coil, heating element and thermostat.

For the 16°C runs the temperature was maintained with ordinary cold tap water circulating in the bath. The flasks containing the reactant solutions were brought to 16° C before a run was made. Dry air was pushed through the observation cell area to avoid condensation on the quartz observation cell.

Temperatures were noted in the bath, before and after entering the cooling area. The fluctuation was never greater than 0.2°C between the inlet and the outlet of the cooling block.

SULFUR REACTANT SOLUTION PREPARATION

The sulfur solutions were made from sodium bisulfite ($NaHSO_3$) at these pH levels: 0.620, 2.50, 3.55, 3.22, 4.02. Weighing solid sodium bisulfite was also the procedure used for all four of the 16°C runs; pH: 0.59, 2.13, 2.09, 3.74.

For the other pH levels (-.301, 1.20, 1.71, 2.11, 2.80, 3.12) SO_2 gas was bubbled into the buffer solution.

TABLE III SHOWS APPROXIMATE FIGURES OF THE AMOUNT (MLS) $NaHSO_3$ ADDED TO A LITER OF BUFFER

TABLE III

pH	Molarity $NaHSO_3$	Ml $NaHSO_3$
0.620	.1 M	5 ml
2.50	.1 M	2 ml
3.55	.01 M	1 ml
4.02	.001 M	5 ml
3.22	.001 M	>1 ml

The concentration of sulfur dioxide was determined by the absorbance of the sulfur solution in the stopped flow apparatus. Wave lengths and extinction coefficients were 270 nm (ε = 461) and 276 nm (ε = 500). The concentrations calculated at the two different wavelengths were always within 3-4% of each other.

Knowing the sulfur dioxide concentration it was possible to calculate the concentrations of bisulfite and sulfite ions by proper manipulation of the known equilibrium constant

expressions.

OZONE REACTANT SOLUTION

Ozone solutions were prepared by bubbling O_3 into the proper buffer with nitrogen from ozone saturated silica gel at -78°. The concentrations were determined at wavelengths of 250 nm and 276 nm. Extinction coefficients were 2430 and 2150 respectively.

BUFFER SOLUTIONS

In the pH range of 2-5 mixture of 0.10m H_3PO_4 and 0.10m KH_2PO_4 solutions were used. The actual pH was found with a Beckman pH meter using the expanded scale. The pH meter was zeroed in with known solutions in the proper pH ranges.

TABLE IV SHOWS THE PERCENTAGE COMPOSITIONS OF THE BUFFER SOLUTIONS

TABLE IV
BUFFER SOLUTIONS
APPROXIMATE PERCENTAGES (0.1M EACH)

pH	% H_3PO_4	% KH_2PO_4
4	2	98
3.5	5	95
3	12	88
2.5	50	50
2	90	10

For pH levels less than 2 0.1-1M H_2SO_4 was used.

OZONE-DIMETHYL SULFIDE GAS PHASE KINETICS

INSTRUMENTATION

The stoichiometric data were obtained using a Packard Model 7300 gas-liquid chromatograph equipped with dual flame ionization detectors, dual electrometers, and a Vidar 6300 Autolab digital integrator. The column employed was a 5' X $\frac{1}{4}$" glass 5% GE XE 60 on Chrom Q. Triple-distilled butyl benzoate was utilized as an internal standard for determination of product yields.

Product indentification was achieved by comparison of product g.l.c. retention times with those of known compounds under identical conditions and by mass spectroscopy using a Varian Mat III GS/MS system.

APPARATUS

A Welsbach T-408 electric discharge ozonator was used to produce the ozone. The ozone flow rate was determined by passing the ozone-oxygen (nitrogen) stream through a potassium iodide solution for a known time and titrating the solution, on acidification, with a .005 N solution of sodium thiosulfate.

The equation for the flow rate is:

$$\frac{N \cdot V \cdot .024}{t \cdot .48} = \text{moles } O_3/\text{min}$$

V = milliliter of $Na_2S_2O_3$ used
N = normality of $Na_2S_2O_3$ used
t = time in minutes that O_3 was passed into KI trap

In this study, the carrier gas was simply passed through the Welsbach ozonator, split to decrease the ozone concentration, brought to the desired temperature of either 25°C of

35° C and introduced into the mixing chamber.

The ozone stream was split in order to decrease concentrations to those desired. Attempts to decrease ozone concentrations to those required by decreasing the current on the ozonator yielded inconsistent ozone flow rates.

After the ozone stream was split, the flow rate of the resulting stream was measured by a Fischer and Porter "Tri Flat" rotometer. The nitrogen flow rate was determined by a Gilmont Model R795 rotometer.

Dimethyl sulfide was introduced into the nitrogen stream by a .1 ml Hamilton gas-tight syringe drived by a Sage model 341 syringe pump. Flow rates for the DMS were varied from .0003 to .00006 ml/min.

DMS-O_3/O_2 Reactor System

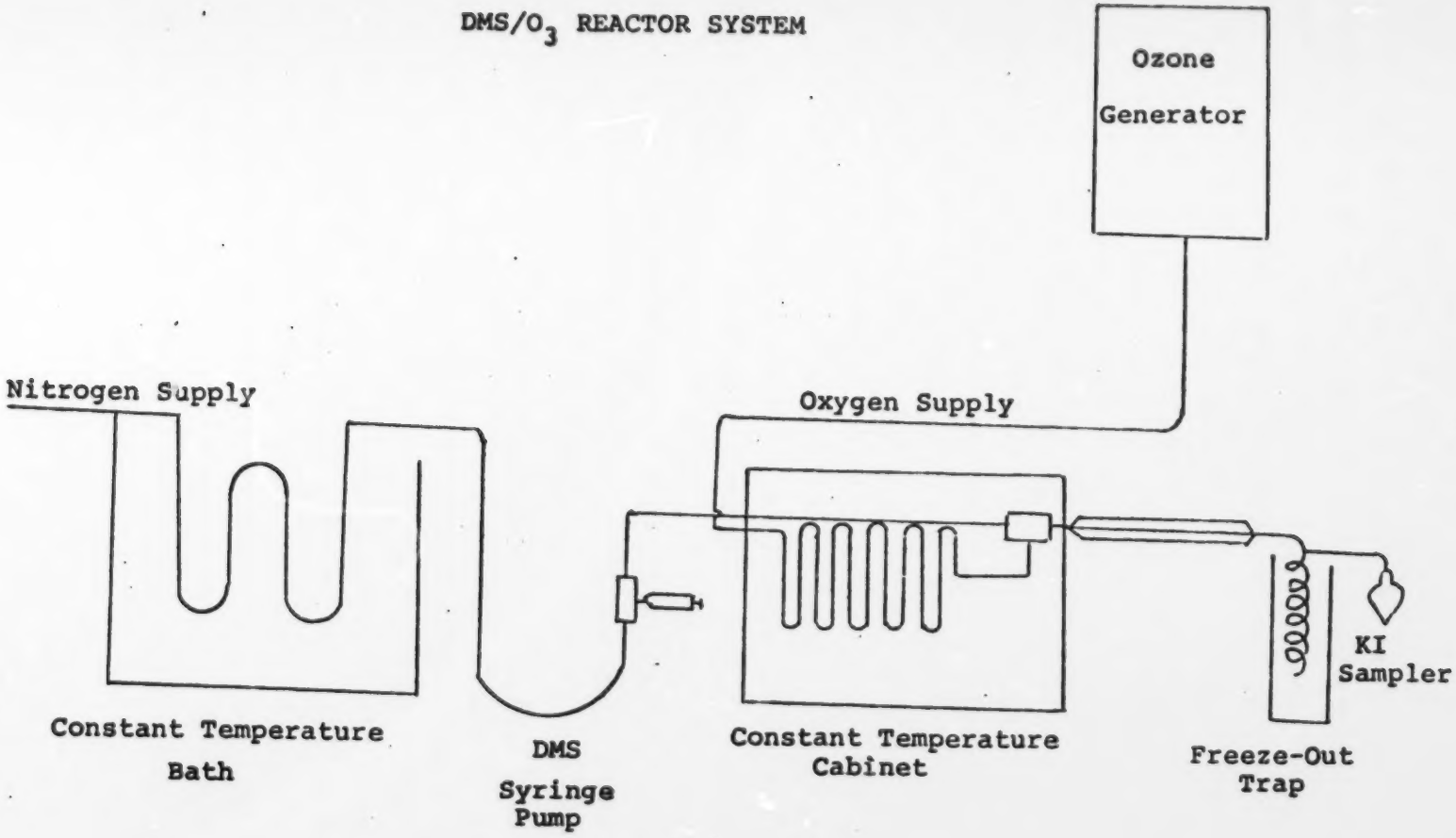
Before the DMS was injected, the nitrogen stream was brought to the desired temperature in a constant-temperature water bath. In order to achieve complete DMS vaporization and to prevent the liquid DMS from splashing on the walls, the injection chamber was expanded, the diameter of the glass tubing carrying the nitrogen was decreased and the end was splayed. After injection, both the N_2/DMS and the O_3/O_2 streams entered a styrofoam constant temperature cabinet, passed through 1' and 17' of glass tubing respectively, came together in the gas mixing chamber and then entered into the reactor. The mixing chamber was designed according to Hale's specifications[22] and consisted of a Teflon collar mounted within a stainless steel sleeve. The O_3/O_2 stream passed into the sleeve and proceeded into the reactor through four .5 mm radial holes drilled into the collar. The boundaries between the collar and the sleeve were kept gas-tight using Vitron "O" rings. The reactor was constructed of precision-bore Pyrex tubing having an inside diameter of 1/8" $\pm$ .0002"

and had an inside volume of 1.988 millliliters. The reactor temperature was controlled by means of a water jacket. Figure 1 diagrams the reactor system. Extreme care was taken in cleaning the reactor and associated glassware. The procedure followed for cleaning the reactor was that Hale's[22].

The reaction products were collected by means of a freeze-out trap consisting of a glass spiral connected to an adapted 10 ml pear-shaped two neck flask. Products were then removed from the trap by warming to room temperature and washing three times with three milliliter portions of methylene chloride. A 1 ml volumetric flask was attached to the bottom of the flask in order to obtain accurate 1 ml volumes of CH_2Cl_2-product solutions on evaporation. The trap was immersed in a Dewar containing a solid-liquid slush of n-pentane. Two other solid-liquid slushes were tried; however, tests, proved that product loss resulted when either the dry ice/acetone or the isooctane/liquid nitrogen slushes were used. Since the amount of product was small, the 10 ml of methylene chloride needed to wash out the trap resulted in product concentrations too low to be analyzed. Vapor pressure data for DMSO and CH_2Cl_2 were obtained from Karchmer's[26] The Analytical Chemistry of Sulfur and Its Compounds and from the Handbook of Chemistry and Physics[27] respectively. Extrapolation of Karchmer's data yielded a vapor pressure for DMSO of less than .1 mm of Hg at 0°C. A value of .0896 mm of Hg was obtained using the values of Jose et. al.[28] Methylene chloride's vapor pressure at this temperature was approximately 129 mm of Hg. Since methylene chloride's vapor pressure was almost 1500 times that DMSO's, evaporation without product loss appeared quite feasible as a means of obtaining product concentrations which could be analyzed. This evaporation was carried out by removing the 10 ml flask from the rest of

FIGURE 1

DMS/O_3 REACTOR SYSTEM



the CH_2Cl_2-washed trap and attaching a condenser and a and a nitrogen source. This was then placed in an ice bath and nitrogen was passed over the solution until a volume of 1 ml was reached.

In order to determine the ozone uptake of the reaction, ozone concentrations were measured before and during the reaction by means of a KI sampler attached to the freeze-out trap. It was found that a normal glass frit would hold varying amounts of I_2, causing inaccuracy in the determination of the O_3 concentration. It was not possible to divert the ozone stream in order to wash the frit, since this caused a pressure change and a resulting fluctuation in the ozone flow rate. Studies indicated that it took as long as an hour to restablish the prior O_3 flow. This problem was solved by exchanging the frit with a glass tip consisting of a tapered end and four side openings for a 5-way dispersion of the gas.

Trapping all of the DMS in the freeze-out trap proved impossible. Therefore, the DMS entered the KI solution when the ozone stream was analyzed. DMS reacts with I_2 forming DMSO and $DMSO_2$[26] thereby consuming the I_2 used for ozone concentration determination. Tests determined that adding starch solution to the KI

$$2KI + O_3 + H_2O \rightarrow I_2 + KOH + O_2$$

$$CH_3SCH_3 + I_2 \rightarrow CH_3SCH_3 \cdot I_2$$

$$CH_3SCH_3 \cdot I_2 + H_2O \rightarrow CH_3\overset{O}{S}CH_3 + 2HI$$

$$CH_3\overset{O}{S}CH_3 + I_2 + H_2O \xrightarrow{\text{slow}} CH_3\underset{O}{\overset{O}{S}}CH_3$$

sample while analyzing for ozone eliminated this problem since the starch complexed immediately with the I_2 on its

formation, thus preventing the reaction with dimethyl sulfide. Water was placed in the sampler between KI analysis in order to maintain a constant pressure head.

REAGENTS

Nitrogen

Before entering the reaction system, the nitrogen was further dried and cleaned by passing it through a column packed with a layer of Drierite and silica gel and a layer of 4 Å molecular sieves.

Oxygen

Tests were run on the purity of the oxygen by passing the gas through a Drierite-silica gel column. Extended use indicated a level of purity and dryness sufficient for this investigation.

Dimethyl Sulfide

The Baker grade sulfide was dried over anhydrous calcium sulfate and triple distilled using a 600 mm Vigreux distilling column attached to a 400 mm Claisen-Vigreaux distilling head.

Dimethyl Sulfoxide

The Baker analysed DMSO was stirred at 25°C with 5% of its weight of Darco G-60, filtered, treated with $MgCO_3$ to remove the acidic impurities, stored overnight over CaH_2, and triple distilled through a 400 mm Claisen-Vigreaus column at approximately 10 mm of Hg.

Methylene Chloride

The Mallinckrodt Spectr AR grade methylene chloride was washed with concentrated sulfuric acid followed by dilute sodium hydroxide and finally water. The washed material was allowed to stand overnight over sodium hydroxide pellets and calcium chloride and was then triple distilled using a 600 mm Vigreux column attached to a 400 mm Claisen-Vigreux

distilling head.

Butyl Benzoate

The Matheson Coleman and Bell butyl benzoate was triple distilled using a 400 mm Vigreux column.

All chemicals were analyzed by gas chromatography for purity and stored under nitrogen until needed.

Calibration of Equipment

Calibration of several components of the experimental system was required before runs were made. These calibrations are as follows.

Rotometers

Both rotometers were calibrated using soap-film flow meters. Hales found that on continued use the sapphire rotometer floats picked up static electricity rendering them useless for accurate flow indicators. Therefore, the rotometers were used only as secondary indicators and soap-film flow meters were used for actual gas flow rates.

Syringe Drive

The syringe pump output was calibrated for several settings on ml/hr for a .1 ml Hamilton syringe by measuring the time required for .01 ml of material to be injected. Five settings were calibrated for dimethyl sulfide (see below).

	Setting on ml/hr	Flow Rate
	9	3.2593×10^{-4} ml/min
	8	2.131×10^{-4} ml/min
DMS	7	1.359×10^{-4} ml/min
	6	9.147×10^{-5} ml/min
	5	6.222×10^{-5} ml/min

Determination of Peak Height vs. Concentration Ratios

Gas chromatograph peak height ratios were calculated for DMSO, dimethyl sulfone, and butyl benzoate. On a mole basis these ratios came out to be:

Butyl Benzoate	1.0000
DMSO	.1359
$DMSO_2$	.1788

Evaporation Trap

A known amount of DMSO was added to 10 ml of methylene chloride and evaporated in the trap to a volume of 1 ml. Direct comparison of standard gas chromatographic peak areas with those from the trap indicated a trap efficiency of 99.0 percent.

O_3/O_2 Flow Rate

Since a normal run lasted approximately three hours, tests were run to determine the consistency of the ozone flow over this time period. Due to the slow response of the ozonator, a two hour warm-up period was allowed before samples were taken. Results indicated an average percent deviation of $\pm$2.40 percent. Hales[22] conducted experiments to determine the extent of ozone decay and found that at 28.5°C the decay was less that 1% during a run. Since our flow rates were much higher and the reactor diameter smaller, ozone decay should present no problems.

OZONE-DIMETHYL DISULFIDE AND METHANE THIOL OZONATIONS

ANALYTICAL METHODS

Ozone

The standard iodide-thiosulfate method was used to determine ozone concentrations. Although there recently has been some debate concerning the stoichiometry of the ozone-

iodide reaction,[29-31] the following is generally accepted.

$$O_3 + H_2O + 2I^- \rightarrow O_2 + 2OH^- + I_2$$

The iodine was determined by titration with sodium thiosulfate as shown.

$$2S_2O_3^- + I \rightarrow 2I^- + S_4O_6^-$$

A 100.0 ml aliquot of an aqueous ozone solution was pipetted into a potassium iodide solution. The solution was acidified with 5 ml of 6M HCl and titrated with 0.005 M sodium thiosulfate. Just before the end point, 3 ml of a 0.3% starch solution was added and the titration was continued to the starch end point.

The potassium iodide used was Baker Analyzed and Mallinckrodt AR; both contained less than 0.0003% iodate. Baker Analyzed sodium thiosulfate pentahydrate was used. The crystals were used as a primary standard after determining that the values obtained based on the weight of the crystals agreed within 1.5% of those based on standardization against potassium dichromate.

Methanethiol

Solutions of methanethiol were made by passing the thiol into water and then cooling to the reaction temperature (0°C). An accurately measured aliquot of the thiol solution was transferred to a glass stoppered flask containing 25.00 ml of a known concentration (approximately 0.15 M) iodine solution. After forty minutes, the solution was acidified with 5 ml of 6 M HCl and the remaining iodine was titrated with a standard 0.1 M thiosulfate solution to a starch end point. This method is based on the following reaction.

$$2CH_3SH + I_2 \rightarrow CH_3SSCH_3 + 2HI$$

Methanesulfonic Acid

Potentiometric titrations (Beckman Century SS pH meter) using standard base solutions as titrant were used to determine methanesulfonic acid. The base solutions were standardized against potassium hydrogen phthalate. Ozone was found to interfere with the determination and was removed by bubbling out with nitrogen before the titration.

The methanesulfonic acid was identified by converting it to methanesulfonyl chloride using thionyl chloride. About 2 ml of the suspected sulfonic acid was isolated from the reaction mixture by evaporating the water and refluxing with 20 ml of thionyl chloride for four and a half hours. The thionyl chloride was distilled and the reaction product was identified by coinjection gas chromatography and its mass spectrum.

Sulfuric Acid

The precipitation of barium sulfate from aqueous solutions is the basis for a number of qualitative and quantitative techniques for sulfate. Qualitative tests for sulfuric acid were performed using three techniques. One, a small portion of the solution to be tested was added to a barium chloride solution; the formation of a white precipitate indicates sulfate and the absence of the precipitate indicates the absence of sulfate. For very dilute solutions the formation of a precipitate can better be detected using a spectrophotometer. Two, a small portion of the solution to be tested was used to adjust a Spectronic 20 UV - visible spectrophotometer to 100% transmittance and then a few crystals of barium chloride were added. A decrease in the transmittance indicates precipitation. Three, a drop of a saturated potassium permanganate solution and three drops of the solution to be tested were mixed. One drop of the mixture was placed on a filter

paper which had been impregnated with barium chloride and heated at 70°-80° C for seven to eight minutes. The filter paper was then washed with water and 1 N oxalic acid. If sulfate was present, the precipitated barium sulfate would trap potassium permanganate in its crystal structure. The trapped potassium permanganate would not be washed away; a pink or purple spot indicates sulfate.[33]

Methanesulfinic Acid

Ferric ions precipitate sulfinic acids as shown.[34]

$$3RSO_2H + FeCl_3 \rightarrow (RSO_2^-)_3 Fe^{+3} + 3HCl$$

Qualitative tests for sulfinic acids were carried out by adding 1 ml of 15% $FeCl_3$ to 2 ml of the solution to be tested.

OZONATIONS

Ozone-Gas Streams

An ozone-oxygen stream was passed into a 0°C methanethiol solution in a gas washing bottle equipped with a glass frit. It was found that large quantities of the thiol were removed with the exit gases. Cold traps cooled to -78°C and precipitation as its silver mercaptide were used to trap the escaping thiol. The exit gases from the reaction vessel were passed through an aqueous potassium iodide solution. When ozone passed through the solution as indicated by the formation of iodine, the reaction was stopped and the aqueous solution was extracted with several portions of methylene chloride. The extracts were concentrated by evaporation of the solvent and analyzed by g.l.c. and NMR. The aqueous layer was analyzed for sulfuric, sulfinic and methanesulfonic acids.

Dimethyl disulfide was ozonized by a similar method. Because the disulfide is not very soluble in water, some of the reactions were run on suspensions of the disulfide in

water. Methylene chloride extracts of the resulting solutions were analyzed by g.l.c. Evaporation of the methylene chloride yielded a compound that was distilled under reduced pressure. The compound was characterized by NMR and IR spectra. The aqueous portion was analyzed for sulfuric, sulfinic and methanesulfonic acids.

Ozone Solutions

During the ozonations using gas streams to introduce ozone, it was found that large quantities of methanethiol or dimethyl disulfide were lost in the gas streams. Therefore, in order to obtain quantitative results solutions of the thiol or disulfide were added to an ozone solution.

About 4000 g of water was weighed and cooled to 0°C, for use in the preparation of an ozone solution. Both ozone-oxygen and ozone-nitrogen streams were employed to make the solution. Methanethiol solutions prepared as previously described were made while the ozone solution was being prepared. Because of the instability of the solutions, the following procedure was carried out as rapidly as possible. An aliquot of the methanethiol solution was added to an iodine solution for analysis of the thiol. The initial ozone determination was started by adding an aliquot of the ozone solution to a dilute potassium iodide solution. Then an aliquot of the thiol was added to the ozone solution and stirred slowly for approximately a minute to insure complete reaction and mixing. Two aliquots of the reaction mixture were then added to potassium iodide solutions for determination of the final ozone concentration. In the initial experiments an aliquot of the reaction mixture was then used to determine the methanesulfonic acid. For reasons described later, it was necessary to remove the residual ozone before titrating. The ozone was removed by bubbling with nitrogen until a small sample of the reaction mixture would give no color when

added to a potassium iodide-starch solution. The quantitative work on dimethyl disulfide was done using the same procedure. The disulfide was used as a primary standard in making up solutions and was not analyzed.

SECTION V

DISCUSSION AND RESULTS
SULFUR-DIOXIDE OZONE

The various species of sulfur dioxide in aqueous solution are shown in equation 1.

$$(1)\quad SO_2 \overset{H_2O}{\rightleftharpoons} SO_2 \cdot H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons HSO_3^- + H^+ \rightleftharpoons SO_3^= + H_2^+$$

It was our initial assumption that each of the species-sulfite, bisulfite, and sulfurous acid (or aqueous sulfur dioxide) was capable of reacting with ozone. To distinguish among these possibilities we measured the rate of the ozonation reaction at various hydrogen ion concentrations. Kinetics thus determined yield, for any single pH, an overall rate constant which may include contributions from one or more sulfur species. Equations 2-4 below indicate the reactions which might be occurring.

$$(2)\quad H_2SO_3 + O_3 \xrightarrow[H_2O]{k_{(SO_2)}} H_2SO_4 + O_2$$

$$(3)\quad HSO_3^- + O_3 \xrightarrow[H_2O]{k_{HSO_3^-}} HSO_4^- + O_2$$

$$(4)\quad SO_3^= + O_3 \xrightarrow[H_2O]{k_{SO_3^=}} SO_4^= + O_2$$

Table V shows the mean rate constant ($k_{(\text{total sulfur})}$)

TABLE V

MEAN RATE CONSTANTS

pH	$k_{(\text{total sulfur})}$
- .301	2.24×10^3
0.620	$9.82 \times 10^3 \pm .89$
1.20	$4.31 \times 10^4 \pm .48$
1.71	$1.02 \times 10^5 \pm .35$
2.11	$1.63 \times 10^5 \pm .21$
2.50	$3.03 \times 10^5 \pm .27$
2.80	$4.57 \times 10^5 \pm .37$
3.12	$5.97 \times 10^5 \pm .42$
3.55	$9.47 \times 10^5 \pm .53$
4.02	$1.74 \times 10^6 \pm .66$
	16° Determinations
0.59	$8.60 \times 10^3 \pm .23$
2.13	$1.42 \times 10^5 \pm .11$
3.09	$2.13 \times 10^5 \pm .37$
3.74	$1.43 \times 10^6 \pm .28$

variation with pH at 25.0° and 16.0°. Figure II is a plot of that data, which shows its regularity in graphical form.

Rate constants were determined using the following equation:

$$k = [1/a-b]\,[\ln(b(a-x)/a(b-x))]\,/t$$

where
k = rate constant
a = initial ozone concentration
b = initial sulfur concentration
x = change in concentration at
t = time

Analysis showed the reaction to be second order, first order in both ozone and total S(IV) species.

In order to account for the strong dependence of the rate constant on pH, we have assumed the reaction takes place at different rates with the three species of S(IV) present due to the equilibria

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \qquad K_1$$

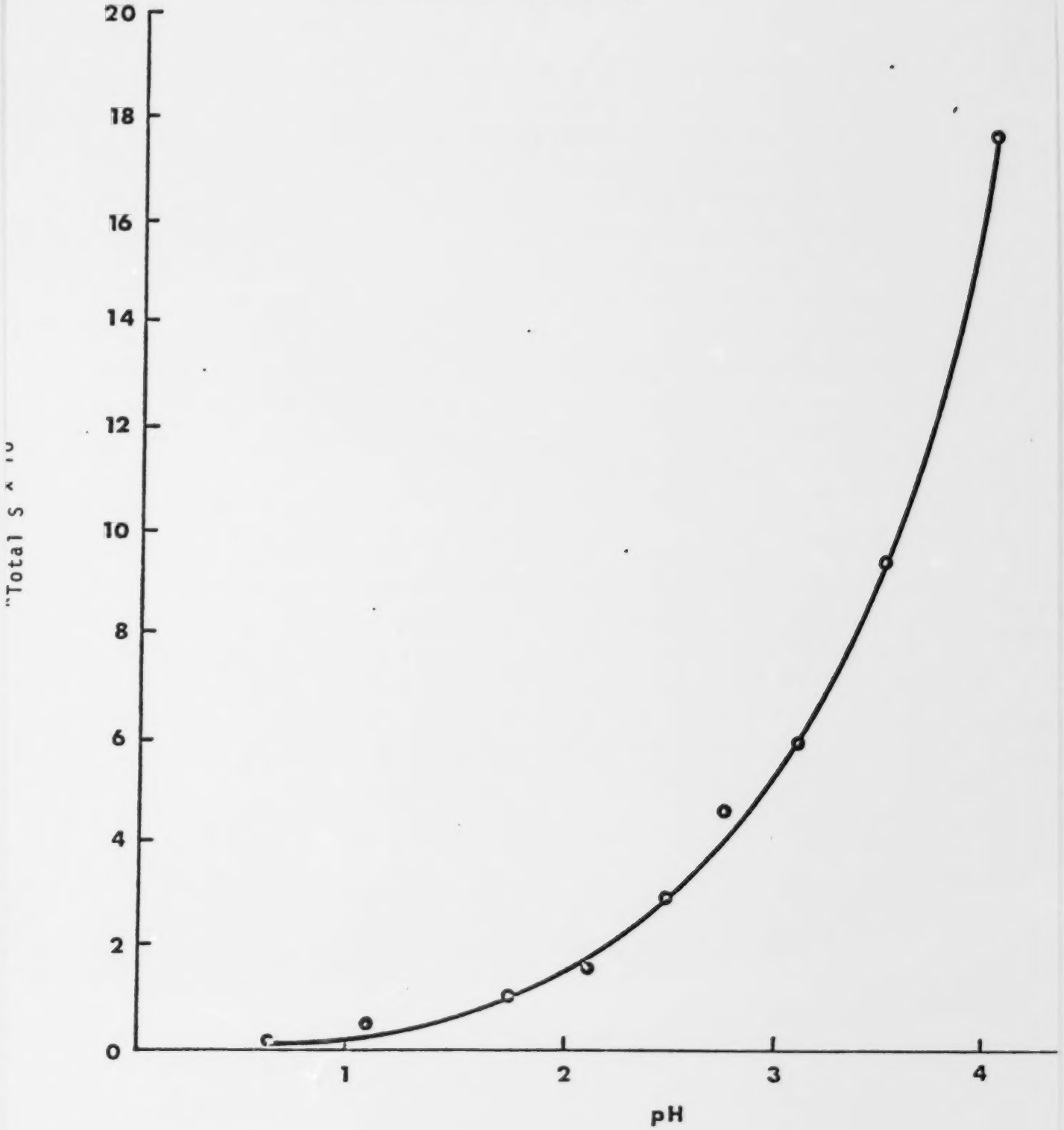
$$HSO_3^- \rightleftharpoons H^+ + SO_3^{-2} \qquad K_2$$

The fractional distribution of the species can be calculated from the pH and the equilibrium constants for the above mentioned equilibria. There seems to be no clear cut choice for the values to be used with values of K_1 reported ranging from 9×10^{-3} to 5×10^{-2} and K_2 ranging from 6×10^{-8} to 5×10^{-6} at 25°C.

Our calculations reported here are based on the K_1 values of Arkhipova et. al.,[35] who report K_1 values at 35°, 25°, and 10° as 1.0×10^{-2}, 1.3×10^{-2} and 1.8×10^{-2} respectively. The K_2 values used are those of Teder who gives values of 1.16×10^{-7} and 9.3×10^{-8} for 25° and 60°. These values were

FIGURE II

DEPENDENCE OF RATE ON pH



chosen because they gave a means of calculating values at temperatures other than those given.

A series of calculations were made using the values $K_1 = 1.72 \times 10^2$ and $K_2 = 1.02 \times 10^7$. Calculated rate constants showed about the same variance but absolute values were different due to the different species distribution calculated.

The sulfur species concentrations were converted into fractions, leading to the equations shown in Table VI. It was obvious that k_{SO_2} was considerably smaller than the other specific rate constants and adds essentially nothing to the overall rate of reaction at hydrogen ion concentrations lower than .1 M. Its fraction of the total sulfur is therefore not included in equations 4-10.

Equations 3-10 in Table VII were used to determine $k_{HSO_3^-}$ and $k_{SO_3^=}$ (computer program using each equation, one at a time, with every other equation, and solving for the rate constants). Those values were then substituted into equations 1 and 2 to determine the value of k_{SO_2}. Similar procedures were followed for the data determined at 16°.

Table VII shows the rate constants thus determined.

Arrheneus treatment reads to the following formulas:

$$\frac{d[HSO_3^-]}{dt} = 10^{14} \exp - \frac{11,600}{RT} [HSO_3^-] [O_3-]$$

$$\frac{d[SO_3^{-2}]}{dt} = 10^{17} \exp \frac{10,500}{RT} [SO_3^{-2}] [O_3]$$

TABLE VI

EQUATIONS FOR CALCULATIONS OF SPECIFIC RATE CONSTANTS

General Equations

$$k_{OBS} = [\text{Fraction } HSO_3]k_1 + [\text{Fraction } SO_3]k_2 + [\text{Fraction } SO_2]k_3$$

	pH	25.0^{o} Runs
1)	-.301	$2.24 \times 10^{3} = .0065\ k_{HSO_3^-} + 3.8 \times 10^{-10}\ k_{SO_3^=} + .993\ k_{SO_2}$
2)	0.620	$9.82 \times 10^{3} = .051\ k_{HSO_3^-} + 2.48 \times 10^{-8}\ k_{SO_3^=} + .948\ k_{SO_2}$
3)	1.20	$4.31 \times 10^{4} = .171\ k_{HSO_3^-} + 3.14 \times 10^{-7}\ k_{SO_3^=} + .829\ k_{SO_2}$
4)	1.71	$1.02 \times 10^{5} = .402\ k_{HSO_3^-} + 2.39 \times 10^{-6}\ k_{SO_3^=}$
5)	2.11	$1.63 \times 10^{5} = .627\ k_{HSO_3^-} + 9.38 \times 10^{-6}\ k_{SO_3^=}$
6)	2.50	$3.03 \times 10^{5} = .805\ k_{HSO_3^-} + 2.95 \times 10^{-5}\ k_{SO_3^=}$
7)	2.80	$4.57 \times 10^{5} = .891\ k_{HSO_3^-} + 6.54 \times 10^{-5}\ k_{SO_3^=}$
8)	3.12	$5.97 \times 10^{5} = .946\ k_{HSO_3^-} + 1.44 \times 10^{-4}\ k_{SO_3^=}$
9)	3.55	$9.47 \times 10^{5} = .979\ k_{HSO_3^-} + 4.03 \times 10^{-4}\ k_{SO_3^=}$
0)	4.02	$1.74 \times 10^{6} = .994\ k_{HSO_3^-} + 1.20 \times 10^{-3}\ k_{SO_3^=}$

TABLE VI (cont'd)

	pH	16.0^{o} Runs
11)	0.59	$8.6 \times 10^{3} = .058\ k_1 + 3.15 \times 10^{-8}\ k_2 + .94\ k_3$
12)	2.13	$1.42 \times 10^{5} = .683\ k_1 + 2.76 \times 10^{-5}\ k_2 + .32\ k_3$
13)	3.09	$2.13 \times 10^{5} = .951\ k_1 + 1.64 \times 10^{-4}\ k_2$
14)	3.74	$1.43 \times 10^{6} = .989\ k_1 + 7.61 \times 10^{-4}\ k_2$

TABLE VII

SPECIFIC RATE CONSTANTS

at 25°

$k_{HSO_3^-}$ = 3.1 ± 1.1 x 10^5 M/1sec

$k_{SO_3^=}$ = 2.2 ± 1.6 x 10^9 M/1sec

k_{SO_2} = 5.9 ± x 10^2 M/1sec

at 16°

$k_{HSO_3^-}$ = 1.71 ± .3 x 10^5 M/1sec

$k_{SO_3^=}$ = 1.3 ± .7 x 10^9 M/1sec

k_{SO_2} ≅ 0 M/1sec

from which the reaction rate at any temperature can be calculated. The overall reaction rate will be the sum of the two rates determined by calculating the concentration of each species from the equilibrium constants and the pH.

The contribution of the $SO_2 \cdot H_2O$ species to the rate is small at all pH of interest in the atmosphere. Our value of less than $10^{-2} \times k_{HSO_3^-}$ would make the contribution of this species less than 1% of the total rate at all pH values more than 1.7.

Conversely, the SO_3^{-2} species becomes a greater than 1% contributor when its fraction becomes greater than about 10^{-6} since its rate constant is about 10^4 x that of the HSO_3^- species. This occurs at about the same pH (1.7) that the SO_2 species becomes unimportant. Thus below pH 1.7 we can ignore sulfite contribution and above this pH we can ignore the SO_2 contribution to the rate. At pH > 4, the reaction is almost entirely due to SO_3^{-2}.

Because of the extreme dependence of rate on pH (rate approximately doubles for 0.5 pH change), the method of dividing the overall rate constant into the specific rate constants for the different species is valuable. The distribution among species is a function only of the H^+ concentration and the ionization constants of the species involved so our rate constants can be used to determine an overall rate constant at any desired pH.

There were experimental difficulties in working at the hydrogen ion concentrations of atmospheric interest. The problems. were:

(1) Increasing the pH decreases the amount of sulfur dioxide in solution (bisulfite becoming the common sulfur species present under our conditions). This meant that either we increase total sulfur, in order to have relatively constant absorption

of sulfur dioxide for the determination of initial concentrations or work at lower accuracies with respect to all concentrations. We chose to keep relatively high sulfur dioxide concentrations. In retrospect (see 2&3) our choice was wrong.

(2) The rates of ozonation increased dramatically with increasing pH. This meant that at higher pH values our kinetic results started to be limited by the mixing time of the stopped flow apparatus. For the 16° runs concentrations of both ozone and total sulfur were lowered for higher pH runs, but the determinations above pH 3 at 25° are suspect.

Because of that (after the termination of the grant) we lowered the concentration of ozone by a factor of 20 and the concentration of total sulfur by a factor of 80 and did one more determination at pH 3.22. The observed rate constant (1.79×10^6) was almost three times larger than what we would have expected from extrapolation on Figure II. The result by itself does not indicate whether we had pushed the limits of the stopped flow apparatus previously or whether our decreased accuracy of measuring total sulfur was responsible. In fact we think it likely that a third factor (3 below) may have been important in both that experiment and in all kinetic determinations at higher pH.

(3) Our basic assumption has been that equilibrium occurs in the conversion of one sulfur species to another. Using the rate constants from equation 5 it can be shown that equilibrium would be established rapidly enough so that ozonation can occur with each species at most concentrations used. However, at high pH and with very high concentrations of total sulfur and ozone the rate of formation of sulfite from sulfurous acid is only about ten times that of its disappearance from reaction with ozone. This seems <u>not</u> to

be a particularly bad problem since at such acidities most of the total sulfur is already in the bisulfite form. More serious is our original assumption that the rate constants for the second step of the ionization

$$HSO_3^- \underset{k_{-2} \cong 10^{11}}{\overset{k_2 \cong 10^4}{\rightleftharpoons}} H^+ + SO_3^=$$

has the values shown. We have found no mention of these rate constants in the literature and have assumed them from a) knowing the equilibrium constant and b) guessing that the recombination of a proton with sulfite ion might have about the same rate constant as the similar reaction between sulfate ion and a proton (a diffusion controlled reaction rate). At pH above about 2, the SO_3^{-2} rate is important. The above assumed rates would indicate that SO_3^{-2} is being used up more rapidly than it can be replenished by HSO_3^- dissociation. This would result in a trend similar to that observed of an apparent relative decrease in the constant with the increase in pH.

Environmental Implications

The reason for determining the kinetics of the reaction between ozone and sulfur dioxide in solution was to discover whether such a reaction might take place under normal atmosphere conditions. While this study was in progress, Penkett determined the rate of the reaction between bisulfite ion and ozone and reported the following results.[11]

a) The reaction is rapid, having a second order rate of

$$\frac{dO_3}{dt} = [3.32 \pm .11 \times 10^5 M^{-1} \text{ sec}^{-1}] [O_3] [HSO_3^-]$$

at 9.6° and at a pH of 4.65.

b) Using reasonable atmospheric conditions [SO_2 in atmosphere = 0.007 ppm, O_3 - 0.05 ppm, clouds contain 0.1 to 1 g liquid water per cubic meter, bisulfite concentration in solution = 5×10^{-5}] he calculates an oxidation rate of 12.6% hr^{-1}. He notes that his is 70 times the rate of disappearance of sulfur dioxide via oxygen.

Our results are in conflict with those of Penkett on several counts. First we note that the pH dependence of the reaction is such that there seems to be little doubt that Penkett measured the rate of the sulfite ion-ozone reaction as a major part of his rate constant. Since his ozone solution was unbuffered and at a pH of 4 and his bisulfite concentration varied between 10^{-4} and 10^{-5} the exact pH (and therefore the exact sulfite ion concentration) must have been slightly variable. We have retabulated his rate constant variations with bisulfite ion concentration in Table IX.

Table VIII

Rate Constants Ozone-bisulfite (Penkett)

conc HSO_3 (M)	k
10^{-5}	5.7×10^5
2.5×10^{-5}	3.48×10^5
5.0×10^{-5}	3.46×10^5
10^{-4}	3.27×10^5

If Penkett's initial pH were 4.65, as he suggests, then the normal prediction would be that the solution with least buffering capacity (the 10^{-5} solution) would be at the lowest pH when mixed with the ozone solution at pH 4.

Our initial prediction would have been that rates would increase with increasing bisulfite ion concentration since the highest pH solution would have the highest sulfite ion concentration. The trend of Penkett's data is clearly in the other direction. The highest rate is found with the lowest initial concentration of bisulfite.

However when the major discrepancy of our work with Penkett's is considered, a possible explanation for his upward trend in rates with decreasing bisulfite may be given. Specifically, our rate equation predicts that the second order rate constant for Penkett's conditions should have been 5.5×10^6, using $HSO_3^- = 10^{-5}$ M. His value of 5.7×10^5 would therefore be too low by a factor of about 10, while his "average" rate constant (3.32×10^5) is about 15 times lower than what we would predict.

We believe that Penkett's upward trend in rates with decreasing bisulfite concentrations, our own similar finding, and the fact that our predicted rate constants are considerably higher than his experimentally determined values, have the same cause. Specifically, sulfite can react with ozone only if it is formed rapidly enough under equilibrium conditions to do so.

For purposes of comparison, let us assume the same concentrations as Penkett did: SO_2 at 0.007 ppm, ozone at 0.05 ppm, .1 gm per m^3 liquid droplets of water, pH = 5.0, and a temperature of 10°C. Using the activation energies obtained in this work we can extrapolate values for $k_{HSO_3^-}$ and $k_{SO_3^=}$ of 1.1×10^5 $(M/l)^{-1}$ sec^{-1} and 7.4×10^8 $(M/l)^{-1}$ respectively.

Using the values of $K_H = \dfrac{M_{SO_2\,(aq)}}{P_{SO_2\,(g)}} = 2.20$ and

$$K_1 = \frac{(H^+)\ (HSO_3^-)}{(SO_2\ (aq)\ )} = .0184$$ from the work of Johnstone and Leppla (1934) we arrive at a HSO_3^- concentration of 4×10^{-5}M and a $SO_3^=$ concentration of about 4×10^{-7} M. and an ozone conc. of 10^{-9} M. Therefore,

$$-\frac{dS_{(IV)}}{dt} = (1.1 \times 10^5 \times 4 \times 10^{-5} + 7.4 \times 10^8 \times 4 \times 10^{-7}) \times 10^{-9}$$

$$= 3. \times 10^{-7}\ (M/1)\ \text{sec}\ -1$$

For each M^3 we have 1×10^{-4} 1 of solution so we now obtain 3×10^{-11} moles/m^3/sec reacted or 1×10^{-7} moles/m^3 hr or 6.4×10^{-6} g/m^3 hr.

The starting concentration of .007 ppm gives 20 mg m^{-3} so $\frac{6.4}{20}$ = .32 or 32% per hr is reacted. Penkett arrived at a figure of 12.6% per hr. This difference is partially due to the apparently different values used for K_H and K_1 (He calculated a concentration of $HSO_3^- = 1 \times 10^5$). Another possible contributing factor may lie in the precision of our activation energy and the consequent uncertainty of the extrapolated values for the specific rate constant. All of the above calculations assume that solution is rapid enough that equilibrium between the various phases and species is maintained.

Comparing the above rate with rates published for other oxidation modes, it must be concluded that, for the cited conditions (liquid droplets, presence of ozone at a constant concentration) ozone caused oxidation is an important contribution to the oxidation of S(IV) in the atmosphere. For example, Brimblecombe and Spedding[36] using approximately the same total S(IV) and H_2O (l) values that we assume, calculate the

removal of about 3% per day by the Fe (III) catalysed oxidation by atmospheric oxygen, Cheng et. al.[37] calculate a 2%/hr decrease in sulfur dioxide in natural fog in the presence of manganese salts and Sidebottom et. al.[38] show a 1.9%/hr loss of sulfur dioxide photochemically at high humidity.

METHANETHIOL-OZONE

Methanethiol-General Results

When an ozone oxygen stream was passed into a 0°C aqueous solution of methanethiol, a rapid reaction occurred. Quantitative analysis was not possible using this system because large amounts of methanethiol were carried away in the oxygen stream. Cold traps were not effective in trapping all of the escaping thiol, but silver ions were found to precipitate all of it. Since the determination of the amount of thiol precipitated was not practical, an indirect method of analysis was attempted. A known amount of silver nitrate was used to trap the escaping thiol and the excess silver was titrated with potassium thiocynate. Unfortunately, absorption of silver ions on the precipitated mercaptide obscured the end point. Therefore, the reaction was usually stopped when the thiol concentration was so low that some of the ozone passed through the solution without reacting.

A strongly acidic solution resulted from the reaction; however, qualitative tests for sulfuric and methanesulfinic acids were negative. The acidic product was isolated and it was identified as methanesulfonic acid by conversion to methane-sulfonyl chloride. Extraction with methylene chloride revealed that other products were also present. Dimethyl disulfide, methyl methanethiosulfonate and methyl methanethiosulfinate were identified as minor constituents. The disulfide and thiosulfonate were identified by coinjection gas chromatography and their mass spectra. The thiosulfinate was shown to be present by gas chromatography and nuclear magnetic resonance resonance spectra. Continued ozonation resulted in the formation of sulfuric acid. The equations

below summarize the chemical processes:

$$CH_3SH + O_3 \rightarrow \begin{cases} CH_3SO_3H + CH_3SSCH_3 \\ CH_3SO \cdot SCH_3 \\ CH_3SO_2SCH_3 \end{cases} \text{(trace)}$$

$$CH_3SO_3H + O_3 \xrightarrow{\text{slow}} H_2SO_4$$

The stoichiometry of this reaction was studies by adding known thiol solutions to known ozone solutions. The results obtained are given in Table X. The results indicate a stoichiometry of slightly less than 2 moles of ozone per mole of thiol. No difference in stoichiometry was found, whether ozone-oxygen or ozone-nitrogen streams were used to prepare the ozone solutions.

Titration of the resulting sulfonic acid was not straightforward. When a sample was titrated immediately following reaction, the titration curve contained two inflection points. The first inflection corresponded closely to quantitative conversion of the thiol to sulfonic acid. If the solution was allowed to stand several days before it was titrated, a single inflection point having a value equal to that of the second inflection in the original solution was obtained. It was found that if the excess ozone was removed before titrating, only one inflection point was obtained and it corresponded to near quantitative conversion of the thiol to sulfonic acid. The yield of sulfonic acid was taken at the first inflection point was obtained and it corresponded to near quantitative conversion of the thiol to sulfonic acid. The yield of sulfonic acid was taken at the first inflection point or from a titration in which the excess ozone had been removed. The yields obtained are also given in Table X.

The rate of the reaction appeared to be very fast.

TABLE IX

Run	Moles of O_3 Consumed	Moles of CH_3SH Added	O_3/ CH_3SH	Moles of CH_3SO_3H Produced	% Yield
1	1.24×10^{-3}	6.30×10^{-4}	1.97	6.36×10^{-4}	101
2	1.18×10^{-3}	6.84×10^{-4}	1.75	6.87×10^{-4}	100
3	#9.7×10^{-4}	5.58×10^{-4}	1.74	5.54×10^{-4}	99.3
4	#4.3×10^{-4}	2.38×10^{-4}	1.80	2.74×10^{-4}	115
5	1.03×10^{-3}	5.97×10^{-4}	1.73	7.40×10^{-4}	124
6	9.6 xx 10^{-4}	5.73×10^{-4}	1.68	----------	----
7	#----------	1.65×10^{-4}	---	1.71×10^{-4}	*103
8	#1.82×10^{-3}	1.03×10^{-3}	1.76	1.02×10^{-3}	98.5
				1.09×10^{-3}	*106

- Solution made with ozone-nitrogen stream.

* - Yield determined after removal of excess ozone.

Observation of the decrease in ozone was followed spectrophotometrically at 285 nm using the stopped flow apparatus. At initial thiol concentrations of 7×10^{-5} M. and ozone concentrations of 3×10^{-4} M the reaction was over in about 0.1 seconds.

The experimental titration curves show a double hump pattern obtained when an aliquot of the reaction mixture is titrated in the presence of ozone. However if the ozone is removed a standard titration curve is obtainable. This pattern, although puzzling at first, proved to have a simple explanation. In basic solutions, ozone will react with methane sulfonic acid to produce sulfuric acid much faster than in acidic solutions. In acidic solutions, the reaction proceeds very slowly. That is why letting the solution stand for several days results in a single hump pattern corresponding to the second hump in a titration with ozone present. As the equivalence point is reached during titrations with ozone present, the pH rises allowing sulfuric acid to be produced at a reasonable rate. The pH then remains relatively constant until the ozone has all reacted. Tests with methanesulfonic acid showed the same behavior as the reaction mixtures. Other tests demonstrated that sulfate was formed when ozone was added to basic solutions of methanesulfonic acid.

Methanethiol-Errors

Any quantitative measurement is subject to some error. The results given in Table X exhibit some random error. The stoichiometry from run #1 and the yield from run #5 are more than two standard deviations from the mean and, therefore, have been dropped from the respective calculations.

Doing this one obtains a stoichiometry of 1.74 ± 0.04 and a yield of 103% ± 6%. The limits of error given are one standard deviation.

This treatment of random errors does not include any systematic errors. Although efforts were made to reduce any error of this type, several sources of possible error exist. The solutions used in this study were all unstable with respect to loss of the solute into the air. In order to minimize this type of error, initial concentrations were measured, the reaction was carried out and final concentrataions were measured as rapidly as possible. Ozone is also known to undergo thermal decomposition, but this is a slow reaction compared to the time between samplings (about one minute).

Because of the limited solubility of ozone in water, the solutions used were very dilute. Final ozone concentrations ranged from 5×10^{-5} to 3×10^{-4} M. At these concentrations, end points were not extremely sharp. This was particularly a problem in the sulfonic acid determinations where the steep portion of the titration curve generally occurred in 1/4 to 1/2 milliliter.

Methanethiol- Scientific Implications

The reaction of ozone with methanethiol has been shown to produce methanesulfonic acid and eventually sulfuric acid. The conversion of the sulfonic acid to sulfuric acid is very slow and, for practical purposes, the reaction stops at the sulfonic acid. When insufficient ozone was added directly to a solution of thiol, dimethyl disulfide, methyl methanethiolsulfinate and methyl methanethiolsulfonate were also detected. The quantitative results seem to indicate that these products were not formed in the reactions carried out

by mixing solutions. This is reasonable because, in the presence of excess ozone, any disulfide and thiolsulfinate would have been oxidized further. However, Barnard[17] has reported that thiolsulfonates are resistant to ozonation. No minor products were detected from these reactions; but at such low concentrations, they may have escaped detection.

These results are not surprising and are similar to the results reported for other thiols. A thiolsulfinate, however, has not previously been reported as a minor product or intermediate in the ozonation of a thiol. The reason for this probably involved a difference in the mechanism of disulfide ozonations in aqueous and organic solvents. Previous workers using organic solvents have not found thiolsulfinates to be products of long-lived intermediates in the ozone-disulfide reaction. This evidence, although it seems to indicate that the thiolsulfinate is formed from the disulfide, is not sufficient for proof.

Because thiols are readily converted to disulfides, it might be expected that the ozonation of thiols proceeds via disulfides. This does not appear to be the case for methanethiol. If the reaction involved the disulfide, the overall rate would be controlled by the rate of ozonation of the disulfide or the rate of conversion of the thiol to the disulfide, whichever is slower. But methanethiol was observed to react faster than dimethyl disulfide with ozone. Therefore, it must be concluded that disulfide production is only a minor side reaction.

The stoichiometry found is similar to those obtained by Barnard[17] (1.6 O_3:SH) and Erickson (1.6 O_3:iso-BuSH) when the ozone-oxygen streams were passed into the thiol solutions.

Methanethiol-Environmental Implications

The reaction product (CH_3SO_3H) from the ozone-methanethiol reaction is odorless, nonvolatile, and water soluble. These are all positive attributes that could be taken advantage of in designing pollution control equipment for Kraft pulp mills. Although the rate data obtained are in no way complete, it appears that the reaction is fast enough so that no major technological difficulties should be encountered in equipment design. These are some difficulties in using aqueous phase ozonations for pollution control. However, use of ozonized water in the water scrubbers for stack gases or direct gas phase ozonation might be possible.

The importance of this reaction in the atmosphere is hard to judge. In regions where ozone and thiols are present in the atmosphere together, some reaction no doubt takes place. However, these reactions are probably occurring in the gas phase for the most part. In plumes from pulp mills, where suspended water droplets are in high concentration, some aqueous phase reaction may occur if ozone is present.

The situation in the upper atmosphere is similar; if thiols and ozone are both present, some reaction probably occurs, but in the gas phase. Two things should be kept in mind when dealing with the upper atmosphere: 1) it has not been shown that thiols are present there, and 2) other pathways involving the high energy species would compete for any thiol present.

DIMETHYL DISULFIDE-OZONE

Dimethyl Disulfide-General Results

When an aqueous solution of dimethyl disulfide was

ozonized by passing an ozone-oxygen stream into the solution, the major product formed was methanesulfonic acid. The acid was identified by converting it to methanesulfonyl chloride followed by coinjection gas chromatography and determination of its mass spectrum. Methyl methanethiolsulfinate was observed to form in high yield during the beginning of the reaction. In one experiment 0.0056 moles of ozone was added to 0.011 moles of dimethyl disulfide dissolved in two liters of water. The only product detected by NMR spectra of a methylene chloride extract was methyl methanethiolsulfinate. The final pH of the reaction mixture was 5.3. In some runs a small amount of methyl methanethiolsulfonate was also formed. No sulfinic acids were detected. This is summarized in equation .

$$CH_3SSCH_3 + O_3 \rightarrow CH_3SO \cdot SCH_3 \xrightarrow{O_3} CH_3SO_3H$$

The stoichiometry and yields found for the disulfide reaction are given in Table XI. All titrations of the sulfonic acids were performed after the removal of excess ozone from the solution.

The rate of this reaction appeared to be slower than that of the thiol. At initial concentrations of 1×10^{-4} M CH_3SSCH_3 and 6×10^{-4} M O_3 the reaction was observed to be complete in about one half minute.

Dimethyl Disulfide-Errors

The mean stoichiometry and yield found were 3.95 $\pm$ 0.45 and 94.8% $\pm$ 7.1%. Eliminating runs more than two standard deviations away from the mean gives 3.89 $\pm$ 0.07 and 95.6% $\pm$ 4.0%.

This reaction was carried out using the same procedure as the thiol reaction, and the limitations of the method are the same. One additional problem was encountered,

TABLE X

Run	Moles of O_3 Consumed	Moles of CH_3SSCH_3 Added	O_3 / CH_3SSCH_3	Moles of CH_3SO_3H Produced	% Yield
1	*2.24×10^{-3}	5.63×10^{-4}	3.97	1.16×10^{-3}	103
2	*2.17×10^{-3}	5.63×10^{-4}	3.84	1.13×10^{-3}	100
3	2.68×10^{-3}	5.63×10^{-4}	4.77	1.10×10^{-3}	98.1
4	2.15×10^{-3}	5.63×10^{-4}	3.82	1.04×10^{-3}	92.2
5	2.21×10^{-3}	5.63×10^{-4}	3.92	9.37×10^{-4}	83.2
6	1.90×10^{-3}	5.63×10^{-4}	3.38	1.04×10^{-3}	92.2

* - solution made with an ozone-oxygen stream.

however. The time necessary for completion of the reaction was not considerably less than the time allowed for reacting. Although enough time for complete reaction was generally allowed, it is remotely possible that some reactions were stopped before completion. Longer reactions times were avoided because of the instability of the solution.

Dimethyl Disulfide-Scientific Implications

There appears to be a difference in yield of sulfonic acid between reactions run with solutions made from ozone-oxygen and ozone-nitrogen streams. Considering the limited amount of data and the large degree of scatter, it is possible tnat this apparent difference is not real. It is probably best to conclude that ozone will convert dimethyl disulfide to methanesulfonic acid in high yield.

Sulfonic acids have not previously been reported as the products from the reactions of disulfides with ozone, but the formation of sulfonic anhydrides was observed in nonaqueous solvents by Barnard[17]. Although water must be involved at some point in the reaction sequence, the reaction does not necessarily follow the mechanism proposed by Barnard with the addition of a hydorysis step at the end. In fact, the results of the investigation indicate that a different mechanism is in operation. In trying to elucidate the mechanism of the reaction, Barnard[17] conducted experiments in which insufficient ozone for complete conversion was used. Only the normal products of complete ozonation were found. In this study, however, high yields of methyl methanethiol-sulfinate were isolated when insufficient quantities of ozone were used. Apparently in water, the first step of the conversion to sulfonic acid is the oxidation of the disulfide to the thiolsulfinate. Although no sulfonic acid was formed early in the reaction, quantitative data is needed to show that

another reaction pathway going through an undetected intermediate was not in operation. The small amounts of thiolsulfonate that were detected in some runs probably arose through minor side reactions. Known reactions that could possible be the source are:

1) the disproportionation of thiolsulfinate to disulfide and thiolsulfonate, and
2) the autoxidation of thiolsulfinate. It is also possible that the thiolsulfonate is a direct ozonation product.

Dimethyl Disulfide-Environmental Implications

Because methanesulfonic acid is the major product of this reaction as well as from methanethiol, the same advantages (odorless, nonvolatile, and water soluble) in designing pollution control equipment are gained. The slower reaction rate would make removal of the disulfide more difficult.

The opportunity for reactions in the atmosphere are the same as those for the thiol.

DIMETHYL SULFIDE-OZONE

Over a year's work went into the building of gas phase kinetic system, and many months of obtaining rate data followed. Although the data is available[37], it is meaningless. Our original system apparently measured the rate of reaction of ozone with dimethyl sulfide which had coo ed out in the freeze out trap. Near the end of the research period several new reaction chambers were built and it appeared as if the reaction was suitable for study.

The last of the reaction chambers was built from non-precision bore 20 mm (OD) tubing and was 120 cm long (Volume = 305 ml). The bend into the KI sampler was considerably less restricted than earlier models. The following data was determined.

Run	Flow (l/min)	$M(O_3)x10^6$	$d(O_3)/dtx10^5$
1	1.260	9.049	1.646
2	1.278	11.362	1.912
3	1.250	7.054	1.103
4	1.261	2.481	.2779
5	1.273	2.724	.3241
6	1.252	6.702	1.242
7	1.259	7.425	1.273
8	1.275	8.797	1.498

Order uncorrected = 1.314
corr. coef. = .995

Run	Flow (l/min)	$M(DMS)x10^5$	$d(O_3)/dtx10^5$
1	1.265	1.462	1.1967
2	1.261	.9874	.7842
3	1.274	.9773	.7080
4	1.267	3.499	1.7399
5	1.272	.6657	.5467
6	1.275	2.276	1.498
7	1.260	2.303	1.646

Order uncorrected = .757
corr. coef. = .974
Correctee Ozone Order = 1.398
Corr. Coef. = .990
Corrected DMS Order = .861*
Corr. Coef. = .969

* This order was computed assuming a 1:1 stoichiometry for ozone and DMS. If the ozone order is assumed to be 1.5 and the DMS to be 1.0, the rate constant at 25° is approximately 4 10^{-2} μ moles/l min. This might be compared to the rate

found by Hales[22] for the gas phase reaction between hydrogen sulfide and ozone of

Repetition of the method at 35° yielded inconsistent results. Specifically ozone concentrations became highly erratic. Whether these problems arose from a faulty ozonator or the method itself is still unknown.

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